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Derivation of Damage Functions for Atmospheric Degradation of Materials

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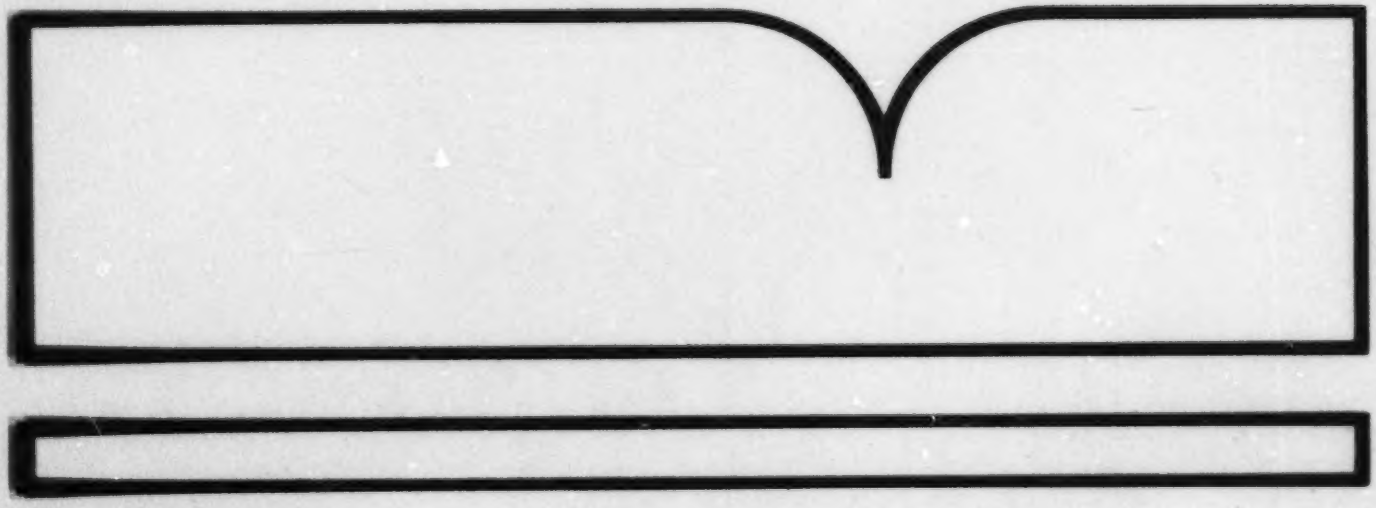

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DERIVATION OF DAMAGE FUNCTIONS FOR ATMOSPHERIC DEGRADATION OF MATERIALS

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The information in this paper is directed to those who develop and use damage functions which relate atmospheric degradation of materials to various causal agents in the atmosphere. Such relationships must be quantified mathematically as part of the overall cost-benefit considerations associated with possible pollution control strategies. Damage functions may be derived from theoretical considerations, from controlled experiments in environmental simulation chambers, from essentially uncontrolled field experiments, or from semi-controlled field experiments. This paper discusses optimum ways of combining these methods to improve the credibility and applicability of materials damage functions for use in assessments, with reference to some of the research performed for the National Acid Precipitation Assessment Program.

INTRODUCTION

One of the adverse effects of atmospheric pollution is the accelerated degradation of man-made and natural materials used in in structures and the accompanying economic costs resulting from reduced service lives. Examples are the erosion of house paints (which may be a precursor to more catastrophic failures such as peeling), accelerated loss of galvanizing on steel leading to rusting, and erosion of stone including loss of carved detail.

This acceleration of normal "weathering" may result in extra maintenance, early replacement of components of a structure, or even complete loss of an art object or failure of a structure. Decisions to control pollutant levels for economic reasons should take such material losses into account, and the appropriate damage functions may be used to help define optimal control strategies.

A damage function is a mathematical expression relating rates of damage or deterioration to causal conditions in the environment. The form of the expression may be derived from theoretical considerations, from experiments, or from

combinations of the two. The coefficients of the damage function must usually be verified from experiments in order to be credible, using two basic methods: laboratory studies or field exposure studies. Each method has advantages and disadvantages, which are discussed in this paper, as is the possibility of field experiments under semi-controlled conditions. As a paradigm for a relatively simple material, some results for zinc (galvanized steel) are presented and applications to other materials are discussed.

There have been many attempts to derive damage functions for materials degradation, notably for metals corrosion, but relatively little attention has been given to systematic experimental designs from first principles. This paper is intended to provide guidance for such an idealistic experimental program design.

REQUIREMENTS FOR DAMAGE FUNCTIONS

For use in economic assessments, damage functions must be credible and widely applicable. Credibility requires a number of elements in order to satisfy potential users: 1) consistancy with underlying theory, 2) verification under realistic ambient conditions, encompassing the conditions under which the functions will be used, and 3) statistical robustness of the verification data. Of course, as in all real world projects, all of this must be accomplished within finite time and budget constraints.

The applicability of a damage function is related to its completeness. Strictly speaking, only the pollutants that are subject to possible future controls need be included. Interactions of many pollutants, however, are often subtle and difficult to detect with field experiments of limited scope. For example, SO_2 and suspended particulate matter (TSP) are often covariant. A damage function that fails to separate the effects of these two agents will not be universally applicable. Since there are many interacting agents in the environment, this requirement, which is related to statistical robustness of field data, can lead to a need for expanded field verification programs.

Three-Step Damage Function Development

With benefit of a certain amount of hindsight it is possible to formulate an optimal way to combine theoretical and experimental approaches. Theory can be used to postulate the appropriate mathematical forms for given materials, leading at best to a complete theoretical model requiring only field verification of coefficients. At the very least, theory may be used to predict which agents are likely to be important and what forms of damage might result (pitting, erosion, cracking, etc.). It is also important to establish the proper mathematical form (linear, exponential,etc.) to which statistical analysis of field data should be applied.

For some materials, theoretical information may be limited, and laboratory experiments as a second phase in damage function development may be needed. Environmental simulation chambers are perhaps the most cost-effective way to rapidly screen for the most important direct and interacting pollutant effects. Often, it is necessary to sacrifice some environmental realism to get quick answers. These quick answers, however, may considerably reduce the needed scope of field test programs.

The third step in the ideal damage function development process is the use of field tests to verify theoretical expectations and to supply data to be used to extract the coefficients for the models. The nature of such field tests is highly dependent on the type of damage that is to be predicted and the time history of its development. For example, the process of dissolution or erosion of certain materials may take place quickly enough to allow rates to be determined from analysis of the chemistry of precipitation runoff. In such cases, causality may be infered from time series analysis of material losses versus pollutant input.

For forms of damage requiring substantial time to develop, such as paint film failure by substrate metal corrosion, large numbers of potentially important variables confound the analysis of field test data. Each instance of failure will constitute an observation and, in general, we like to have at least five times as many observations as possible explanitory variables. It is in such cases that preliminary investigations in chambers or by theoretical means can have a large payoff.

DERIVATION OF THEORETICAL FUNCTIONAL FORMS

Most measures of degradation have been observed to increase with time. "Delayed failures", however, may not be observable until some specific amount of time has passed. In those cases, time to failure becomes a measure of the rate of degradation. Time per se,however, is never a causal factor. The rates at at which physical and chemical processes occur control the rates at which measures of degradation can be observed.

Basic Processes

One of the most generally applied time functions for metals in a specificset of environmental conditions has the form[1,2,3]:

$$C=At^n \qquad (1)$$

where C is a measure of corrosion loss,t is time, and A and n are empirical coefficients. The exponent, n, usually has a value between 0.5 and 1.0.

This empirical form is consistent with competing mechanisms of formation and dissolution of protective corrosion product films[4]. The solution to the differential equation describing this process is the transcendental function:

$$C = bt + a[1 - \exp(-bC/a)]/b \quad (2)$$

which is equivalent to:

$$C = bt + a/(dC/dt) \quad (3)$$

The coefficient b represents the rate of dissolution of the protective film which is a function of the rate of delivery of dissolving pollutants to the surface. The coefficient a is a function of diffusivities through the film which can also be affected by pollutants incorporated into it.

When bC/a is large, exp(-bC/a) approaches zero and the function becomes linear: a/b represents the intercept and b represents the slope. The intercept is proportional to the steady state thickness whenthe rate of dissolution of the film is equal to the rate of formation. After only a few months of exposure in a polluted atmosphere, zinc or galvanizing on steel has this corrosionbehavior[5,6], which makes this material a good candidate for a paradigm of a relatively simple system for analysis.

Theoretical Effects of Dry and Wet Deposition on Zinc

Zinc corrosion is believed to be stoichiometrically proportional to the amount of SO_2 deposited on the surface during periods of wetness [3,6]. With accumulated SO_2 expressed as micrograms deposited per square centimeter and corrosion express as micrometers, the theoretical coefficient is 0.00143.

Rain can dissolve the protective zinc carbonate film that forms on galvanized steel[5]. The solubility of zinc carbonate is proportional to the concentration of CO_2 in solution[7] which in turn is proportional to the atmospheric levels of CO_2. Since the solubility of CO_2 in water decreases with increasing temperature[8], a rain effect on corrosion is expected to be negatively related to the rain temperature.

Following a textbook example for the thermodynamics of metal carbonates[9], it can be shown that the overall reaction simplifies to:

$$ZnCO_{3(c)} + H_2O_{(1)} + CO_{2(g)} = Zn^{++} + 2HCO_3^- \quad (4)$$

The equilibrium equation assuming unit activity for both zinc carbonate and water and an ion balance is:

$$Zn^{++} = (k[CO_{2(g)}]/4)^{1/3} \quad (5)$$

where Zn^{++} is in gm-moles/liter and $[CO_{2(g)}]$ is atmospheres of CO_2 in air. From thermodynamic considerations and solubility data [7,8], the equilibrium constrant k is related to temperature by the relationship:

$$k = \exp(-76.476 + 7035/T + 6.354\ \ln T) \quad (6)$$

where T is absolute temperature in ^{o}K.

From these considerations, a theoretically consistent form of the damage function for galvanizing on steel after about six months is:

$$C = a/b + a_1 t + a_2 SO_2 + a_3 (k[CO_2])^{1/3} R + a_4 R \qquad (7)$$

where t is time and a_1 accounts for the effects of all dry deposited pollutants other than SO_2, SO_2 is the accumulation of SO_2 during periods of wetness, T_r is rain temperature, CO_2 is the ambient level of CO_2, R is the accumulated amount of rain, and the coefficient a_4 accounts for allthe effects of constituents in rain other than CO_2.

The coefficient, a_1, could be a significant factor if other pollutants such as total suspended particulate matter(TSP) or nitric acid contribute to the corrosion of zinc. TSP may deposit on surfaces at any time while the rate of deposition of a gas may be dependent on its rate of reaction with the material. The mechanisms that control the rate of reaction of SO_2 with zinc surfaces may serve as a model for the possible effects of other gases,provided they are equally soluble in water.

During periods of dryness, sulfur dioxide can adsorb on the surfaceof zinc, but without the presence of moisture it does not react to form zinc sulfate. The surface becomes saturated and the net flux of SO_2 to the surface approaches zero. When the surface is wet, however, practically every molecule reaching the surface is quickly consumed by its reaction with zinc to form soluble zinc sulfate. The rate of the reaction (coefficient a_2) is then controlled by the flux of SO_2 to the surface.

The flux to the surface is by the mechanism of turbulent and molecular diffusion through the boundary layer of air flowing over the surface. The flux is thus a function of the size, shape, and texture of the surface as well as windspeed. Using boundary layer theory, fluxes as a function of mainstream concentration and windspeed have been calculated for smooth, small, flat specimens[4,10]. Flux is expressed as the product of "deposition velocity" and the measured mainstream gaseous pollutant concentration. Deposition velocity is simply a coefficient relating flux to concentration, which has the units of velocity. It can be calculated for simple geometries of known surface roughnesses inserted into airstreams of known or assumed velocity profiles. The general form of the relationship is:

$$u = AV^n \qquad (8)$$

where u is the deposition velocity to the surface, V is the wind speed measured or estimated at a point in the airstream relative to the surface wherethe pollutant is also measured, and A and n are coefficients that are dependent on the relative positions of measurements, the surface geometry and roughness, and the mainstream velocity profile.

The general form of the equation for the accumulation of a pollutant on a surface is:

$$P_a = uP_c t \qquad (9)$$

where P_a and P_c are respectively the pollutant accumulation and measured concentration, u is the deposition velocity, and t is either total exposure time or time-of-wetness depending on the nature of the pollutant. Total time is applicable to the deposition of particles and possibly nitric acid; while time-of-wetness is appropriate for most water soluble gases.

The rate of corrosion of zinc increases as the pH of a solution is decreased. Acids not only increase the solubility of corrosion products, but also hydrogen ions are reactants in the cathodic half-cell reaction. The term pH is really a measure of this half-cell potential against a calomel half-cell. It is commonly considered to be the negative logarithm (base 10) of the hydrogen ion concentration of a solution (gram equivalents per liter of solution). Zinc corrosion is proportional to the number of hydrogen ions delivered to the surface, thus, the coefficient a_4 in equation 7 should be a function of pH or hydrogen ion concentration. One can calculate an equivalent amount of zinc corrosion for the amount of hydrogen ions that may be consumed in a cathodic reaction. Thus, if corrosion is expressed in micrometers lost from a horizontally exposed skyward surface and rain is expressed in centimeters, the coefficient a_4 should contain an additive term of 45.8×10^{pH}. Another pH dependent term should be added to include the effect on the solubility of the corrosion product film.

The deposition velocity for particles is much more difficult to estimate than the deposition velocity for water soluble gases. Fluxes to a surface are a function of particle size, shape, and density, and surface orientation, as well as all the factors that affect fluxes of gases[10]. For large particles falling on a horizontal surface, the deposition velocity approaches the terminal velocity of the particles in air. Deposition velocities for sub-micrometer diameter particles toward verticle surfaces may be three or four orders of magnitude slower than for large particles to horizontal surfaces. Thus, estimating the rate of effects of TSP on corrosion requires some knowledge of the particle size distribution as well as the relative concentrations of possible reactive species within that distribution. For example, sulfuric acid aerosols could readily react with zinc if they contacted the surface. However, they are most often found in the sub-micrometer diameter size range which has very low deposition velocities under normal conditions. Therefore, the sulfuric acid aerosol component of TSP is not expected to contribute significantly to the corrosion of galvanized steel. On the other hand, reactive constituants found in the large size fraction are expected to contribute to the corrosion of horizontally exposed surfaces. Constituents that catalyze other reactions may also be an important factor.

Time-of-wetness may be measured using sensors[11] or may be estimated from theoretical considerations and environmental parameters[12,13]. Both techniques are subject to error, but their use is much better than having no estimate of time of wetness. A surface will be wet when the surface temperature is below the temperature at which the vapor presssure of a solution saturated with corrosion products or contaminants is in equilibrium with the relative humidity above it. For pure water the temperature is the dew point. For a saturated solution of zinc sulfate exposed to a 90 percent relative humidity, the critical temperature is 20 degrees Celcius; and at 94 percent it is 5 degrees[8]. For a saturated solution of sodium chloride (sea coasts and Northern roadways) the equilbrium relative humidity of about 75 percent changes very little with changing temperature. Therefore, the definition of time-of-wetness depends on what is on the surface which can change as a function of time and location. Of course, a surface will also be wet when it is exposed to rain,which is often a much smaller percentage of time.

In practice, one can define time-of-wetness as the time during which some specified critical relative humidity is exceeded or it is raining and the surface is not frozen. These criteria are easily applied when measurements are made continuously or on a regular schedule representative of daily changes.

Theoretical Considerations for Other Materials

The corrosion of zinc or galvanizing on steel appears to be a complex process as previously described. It, however, is simple when compared with the corrosion of other metals such as weathering steel, or the degradation of non-metallics such as paints and stone. The corrosion product on weathering steel is relatively insoluble and diffusion of species through the protective oxide film becomes the rate controlling factor[4]. The erosion of the surface of a dense grain marble, like zinc, is a relatively simple system to describe. The intergranular deterioration of calcareous stones and morter, however, are much more difficult to theoretically model. More factors must be considered in the processes and time delays are often associated with observable effects.

The development of theoretical damage functions for paints is complicated by the fact that there are many mechanisms of paint failure. Observable damage for most of these is time delayed. For example, one of the primary reasons for repainting is peeling and cracking. This effect is a function of the paint formulation, the type of substrate, the method of application, as well as the environmental conditions to which they are exposed. One may not be able to detect cracking or peeling for several years and the available methodsfor quantifying the effects may not be sufficiently accurate for pollution damage function development. In such cases, the theoretical development of damage functions may show the necessity for experimental work on

measurement techniques.

Once a damage function for a material such as galvanized steel has been theoretically formulated, the coefficents (as in Equation7) must be verified through experimental programs. Statistically designed controlled environment experiments (chamber studies) are used to simplify this process by separating the possible effects of variables. Field studies are used to confirm that the mechanisms are applicable in the more complex and dynamic real world conditions.

CHAMBER STUDIES

Controlled environment experiments can be performed in contained systems often called chambers. These may be in the shape of boxes, cylinders, or even spheres depending on the parameters that are to be studied. Useful information obtained from these experiments is optimized when they are statistically designed so that both direct and synergistic effects of factors that are expected to be important are observable and separable. In this process, no attempt is made to duplicate real world conditions per se although important factors found in the real world are included in the design. One advantage of chamber studies is that levels of factors can be used that can accelerate the rate of deterioration over real world conditions. Less time is required before measurable damage occurs. Another advantage is that exposure levels can be changed and held constant allowing experimental varibility to be measured. Often, mechanisms of deterioration can be monitored better in a laboratory than they can in the field.

There are two major problems that must be considered when doing chamber studies. First, an important factor present in the real world may be overlooked in the design of the experiment. This excluded factor may not necessarily produce a direct effect but could produce a synergistic effect with some factor that was included. Second,in an effort to accelerate deterioration by changing levels of factors from real world levels, the mechanism of deterioration may also be changed.

When there is little theoretical understanding about different systems, chamber studies can be used to determine which of many possible direct and synergistic effects are significant[14]. A two-level factorial design was used to study effects on several materials including galvanized steel[15]. The pollutant gases, ozone,NO_2, and SO_2 were included in the experiment. Input relative humidity was controlled at two levels. All materials were subjected to a dew/light cycle by chilling them with a chill plate to which they were mounted during a twenty minute period of darkness then exposing them to a xenon arc for twenty minutes. For galvanized steel, only the direct effects of relative humidity and SO_2 were statistically significant (as expected from theory).

Clean air controls for the above experiment revealed a

change in the type of corrosion mechanism for galvanized steel[16]. The relatively short dew/light cycle apparently did not allow the surface to dry completly and form a uniform protective zinc carbonate film. As a result, a large cathode to anode ratio caused severe pitting rather than general corrosion. This indicated that the timing of dew/light cycles in chamber studies is an important factor to consider.

Another chamber study was designed to study the rate controlling factors in the corrosion of zinc by sulfur dioxide and sulfuric acid aerosol[17]. The use of a flow chamber allowed deposition velocities to be determined for both accumulation mode H_2SO_4 aerosols and SO_2 gas at equivalent friction velocities while providing an electrochemical technique to observe corrosion processes in real time. The experiment showed that flux of SO_2 to the surface during periods of wetness was the corrosion rate controlling factor. The deposition velocity of H_2SO_4 aerosols and the resulting corrosion rate of zinc was significantly lower than for SO_2 gas at equivalent concentrations and friction velocities.

Flow chambers attached to a large photochemical smog chamber were used to perform a series of experiments to better define the effects of complex atmospheres that more closely represent real world conditions[18,19]. The smog chamber, operated as a continuous stirred tank reactor, served as a reservoir for the exposure chambers. The process of atmospheric corrosion of galvanized steel was followed by analyzing dew run off and simulated rain washes for possible reactants and products. Concentrations of ozone, NO_2, and SO_2 in the smog chamber were continuously monitored. Other atmosheric constituents were measured periodically. The system was operated at two twelve hour dew/light cycles per day. Some specimens in the exposure chambers were not chilled so they could serve as controls.

Results From Chamber Studies on Zinc and Galvanized Steel

This series of experiments not only confirmed theoretical expectations, but also revealed some new facts about corrosion of zinc in complex atmospheres. Analysis of deionized water washes of control specimens on which no dew was formed confirmed that relatively little SO_2 deposits on zinc when it is dry. The measured amounts were consistent with the adsorption of no more than a monolayer of SO_2. During periods of dew, however, both analysis for corrosion products in the dew and the observation of a significant drop in the smog chamber SO_2 concentration confirmed its expected behavior. There was a one to one relationship between zinc ions and sulfur containing ions in the dew when no other reactions were involved. There was a mass balance between the observed drop in the chamber concentration and the amount deposited on the wet specimens. Deposition velocities calculated using both observations agreed with each other and with deposition velocities calculated using wind velocity profiles in the exposure chambers. These values confirmed that the rate of corrosion of zinc by atmospheric SO_2

during periods of wetness is controlled by the gas phase flux to the surface and is not activation or liquid phase or solid phase diffusion controlled.

The amount of zinc found in wash water solutions of different pH was not only dependent on the hydrogen ion concentration, but also on the concentration of SO_2 to which the dew/light cycle specimens had been exposed. The observations were consistant with the dissolution of corrosion product films with thicknesses inversely proportional to the SO_2 concentrations to which they had been exposed. This behavior confirms the competing mechanisms of buildup and dissolution of corrosion product films.

For the complex smog experiments, measured molar ratios suggest that the dew contains a mixture of $Zn(NO_2)_2$, $Zn(NO_3)_2$, $ZnSO_4$, and $Zn(HCHOHSO_3)_2$. The dominant SO_x species in the dew was $SO_3^=$ in contrast to $SO_4^=$ found in single component SO_2 experiments. It appears that a reaction took place that prevented the complete oxidation to the sulfate. An observed one to one ratio of sulfite to formaldehyde is consistant with the formation of a $HCHOHSO_3^-$ adduct.

Calculated fluxes of NO_2, ozone, and PAN indicate that these species in smog are not significantly involved in the corrosion of galvanized steel. Deposition velocities for both formaldehyde and acetaldehyde during periods of wetness suggest that these species accelerate the atmospheric corrosion of zinc. Nitric acid was found to have gas phase controlled fluxes to the surface during either wet or dry periods. It is probably the reactant most responsible for the nitrates and possibly nitrites found in the dew on the galvanized steel. The contributions of these species should be considered when doing field experiments.

Chamber Studies on Painted Surfaces

The possible effects of three gaseous pollutants on the erosion of relatively simple paint systems have been studied in two chamber experiments[20,21]. Effects of ozone, NO_2, and SO_2 were observed on some paint systems. The most significant effect was the accelerated erosion by SO_2 of paints containing calcium carbonate fillers. The magnitude of this effect was consistant with leaching out of the calcium carbonate. NO_2 caused a weight gain and a brown stain of some white paints. Ozone caused a minor weight loss.

FIELD STUDIES

Most of the existing data on the atmospheric corrosion of metals were obtained from field studies. The American Society for Testing and Materials has been conducting such studies for more than seventy-five years. Only within the last twenty-five years, however, has there been an interest in relating corrosion rates to specific pollutants.

The experimental technique has been to expose specimens for

different periods of time at different locations using standard practices to measure differences in weight change, pit depth, tensile strength, per cent of rust on metallic coated steel substrates, etc. . Earlier experiments did not measure environmental factorsbut classifiedthemintogeneral categories such as urban, industrial, marine, and rural. Within the last twenty-five years there has been a growing awareness of the need to measure environmental parameters in field studies in order to make sense out of the observed variability in corrosion behavior.

Statistical Considerations

In field experiments, because environmental factors vary with time and location, multiple regression techniques are necessary to analyze corrosion behavior. These techniques do not establish cause-effect relationships but infer statistical associations. They also provide unbiased estimates of the parameter coefficients, under proper conditions.

Two basic assumptions are made when using multiple regression analysis; (1) independent variables are free from error and (2) they are not related to each other. Neither is true for the factors that contribute to corrosion. Site selection can reduce covariance, but the existence of physical and chemical relationships between factors makes it impossible to eliminate covariance in ambient environments. The problems associated with independent variable data can be reduced by making sure the the error is small with respect to the differences in factor levels. These are not problems in chanber studies.

The within-sample error of corrosion measurements is relatively small when compared with the measurement errors associated with some environmental factors. The statistical significances of coefficients in a regression are judged against the residual error. The relative error of the least accurate factor having an effect on corrosion will control the relative magnitude of theregression residual error. From theoretical considerations, time-of-wetness is not onlythe most important factor causing corrosion, but is probably the least accurately measured or estimated parameter.

The response of a time-of-wetness sensor is dependent on the type of electronic measurement technique that is used, the type of metal or metals in the sensor, the geometry of the substrate to which the sensor is attached, the chemical pretreatment of the sensor, and its exposure history. To reduce the error associated with this kind of response, one would have to use a sensor made of the same material, with the same size, shape, pretreatment, and exposure history as the metal samples. At this time, this approach is not a practical solution, thus, the existence of these errors must be recognized and data analyzed accordingly.

Errors associated with theoretical estimates of when a surface is wet are not only the result of errors in measuring

temperature, dew point, and/or relative humidity, but also the definitionofthe condensation process. A five per cent error in the measurement of relative humidity or in the definition of critical relative humidity above which a surface is expected to to be wet can cause a forty per cent error in the estimated fraction of the time the surface is wet.

If even large errors are randomly distributed, as length of exposure increases, they tend to cancel out and the estimated average value comes closer to the actual average value. Errors in indpendent variables, however, not only reduce statistical significance but also bias the estimated coefficients downward.

The problems of covariance between "independent" factors and relative differences in their associated errors can lead to erroneous conclusions. In the process of regression analysis, one of several related "independent" variables may be indicated to be statistically significant while the others are not, simply because it has the least error associated with it. Thus, it is possible for a factor that has no cause-effect relationship to serve as a proxy for one that does.

With some understanding of the theoretically expected effects of environmental factors and the nature of statistics it is possible to design field studies that can produce the desired information or determine if the analysis of existing or completed studies can be interpreted meaningfully.

For example, a theoretical SO_2 coefficient for corrosion of zinc at a deposition velocity of one cm/sec, SO_2 in micrograms/m^3, and corrosion in micrometers/year, is 0.045f. The term, f, is the fraction of time when wet. The observed corrosion rate of zinc from all other causes is often around 2f. If f is the major source of error, then minimum difference in ambient average SO_2 concentrations that will causea statistically significant difference in zinc corrosion at the 0.05 probability level is $87E_f$, where E_f is the fractional error associated with the estimate of time-of-wetness. From this analysis, on can calculate that the minimum differences in SO_2 concentrations are 34.8 and 8.7 micrograms per cubic meter for months and years respectively. In the past, site to site differences greater than these were easy to find than they are at present, due to the success we have had in cleaning our air.

In regression analysis, one would like to have at least five times as many data points (degrees of freedom) as there are variables to be evaluated. From theoretical considerations of the simple process of the corrosion of zinc, factors that must be considered and measured are; temperature, dew point, SO_2 concentration, windspeed, H^+ concentration in rain, TSP, time and amount of rain. In addition, chamber studies have identified nitric acid and formaldehyde as possible significant factors. Considering the errors involved in each measurement, a minimum of forty-five data points with exposures of at least a year would be needed to expect to see statistically significant effects

associated with each of these factors. For fewer data points or shorter exposures, only some of the variables are expected to show statistical significance even though all may be causal factors. When environmental factors do not change significantly with time, it may be necessary to consider a site as a data point. Such criteria must be considered in selecting numbers and locations of sites and years of exposure in field test programs.

Field Test Results

One of the most comprehensive extant field studies designed to relate pollutants to materials damage was done in the St.Louis, MO. area in the mid seventies[4,12,22,23,24]. Galvanized steel was one of the materials that was exposed at nine sites in this three year study. Among the factors that were measured at each site were; ozone, oxides of nitrogen, sulfur oxides, total suspended particulate matter (TSP), temperature, dew point, and windspeed. Rain and its constituents were not measured at each site, however, amounts of rain were available from the airport weather station. For the galvanized steel, there were seventeen different exposure periods resulting in a total of 153 sets of data (only seventeen different amounts of rain).

A regression equation based on theoretical considerations could account for better than 97 per cent of the variability in the corrosion of galvanizing on steel. As expected, temperature, dew point (which affects relative humidity and fraction of time when wet), windspeed (deposition velocity), SO_2 concentration, andrain amount weresignificant factors. TSP also contributed significantly to the corrosion of the zinc on steel. Ozone, NO_2, and sulfates and nitrates in TSP were not statistically significant factors. The magnitudes of the regression coefficients were consistent with theoretical predictions. Rain acidity, nitric acid, and formaldehyde were not measured, thus, these possible effects could not be evaluated with this set of data. About half of the rain effect could have been caused by rain acidity resulting from constituents other than carbon dioxide. These results are consistant with statistical studies of many field programs[3] and help explain the intercept found in that work.

Semi-Controlled Field Experiment

More recently, some of the factors of gaseous and wet deposition have been physically separated by using semi-controlled field experiments[25]. An automatic movable covering device excludes rain on half of a set of samples exposed at the relatively unpolluted site at Research Triangle Park, N. C.. Both galvanized steel and weathering steel were exposed in this experiment. For both materials, the direct effect of rain was consistent with the regression coefficients obtained in the St. Louis study. Rain accelerates the corrosion of galvanized steel by dissolving the corrosion product film. The corrosion rate of weathering steel is decreased by rain. Rain

apparantly washes away acids that form and accumulate during periods of dew.

EXPERIMENTAL IMPROVEMENTS

As part of the National Acid Precipitation Assessment Program, the effects of environmental factors on a variety of construction materialsare being studied using both field and chamber experiments. A maintenance paint on hot rolled steel and house paints on wood are included in these studies. Techniques for the early detection of surface degradation are being used and these observations will be subsequently related to the more conventional quantifications of various failure mechanisms. Field sites at Research Triangle Park. NC, (relatively unpolluted with the exception of rain acidity) and Steubenville, Ohio, (relatively polluted) are being treated as semi-controlled experiments. Automatic movable devices exclude natural rain from two-thirds of the samples. A simulated clean rain of equal amount is sprayed on half of these excluded samples. This multiplies the available experimental degrees of freedom for the two sites by three and controls two levels of acid precipitation. For some materials, specimens are mounted both vertically and at 30 degrees from the horizontal. This again adds another level of precipitation and possibly TSP accumulation to the experiment.

Some of the experimental techniques developed in chamber experiments are being used in the field studies. Rain and dew run off from a variety of materials is being analyzed for possible reactants and damage product constituents. Some of these analyses are being done on an event basis so that it will be possible to determine fluxes of pollutants to surfaces during rain, formation of dew, and periods of dryness. These can then be compared with fluxes calculated from measurements of environmental parameters such as windspeed and ambient pollutant concentrations. Results of various techniques can be checked by mass balances.

CONCLUSIONS

Both chamber and field studies are needed to validate theoretical damage functions for use in assessing pollution effects on materials. The example of galvanized steel corrosion behavior demonstrates that chamber studies can be used to establish the mechanisms of cause-effect relationships. Field experiments with the same material show that these relationships are applicable in ever changing real world environments.

The mechanisms of failure of other systems such as paints on different substrates are more complex than zinc corrosion and are much more difficult to study. The basic process in the development of a damage function for use in an assessment, however, is the same. It is, (1) the theoretical derivation of a functional form for a particular failure mechanism, (2) the establishment of cause-effect relationships using controlled environment experiments (chamber studies), (3) and verification

of the applicability of those relationships to real world environments through field studies.

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